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Electrochemical Initiation of Polymerisation

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Publications on the electrochemical initiation of polymerisation are surveyed, and methods are classified on the basis of the mechanism of the electrode reaction in which active centres are formed and the mechanism of growth of the polymer chain. The laws of the electrochemical initiation of radical and ionic polymerisation are analysed, and the advantages and prospects of the latter are shown. The features and possibilities of electrochemical initiation, leading to the formation of linear and network polymers, are examined on specific examples. A list of 138 references is included.

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I. INTRODUCTION

It was established long ago[1] that organic radicals could be formed during electrochemical oxidation or reduction. However, the use of such radicals to initiate polymerisation came only during recent years.

In 1939 Wilson[2] pointed out that reduction by alkali metals occurs in the same way as reduction at a cathode surface, and he suggested that electrochemical initiation of polymerisation was possible. Ten years later Dineen, Schwan, and Wilson[3,4] observed that, at a mercury cathode in acid medium, unsaturated compounds undergo hydrogenation with great difficulty, whereas they are rapidly polymerised. The advantages of such a process are obvious: the species responsible for initiating polymerisation are formed by an electrode reaction, so that the rate of initiation can be controlled very simply by varying the current density. It can be maintained constant or varied in pulses, which may yield a polymer having a narrow molecular-weight distribution.

Published information[5-8] indicates that electrochemical initiation may play a significant part in the solution of such important problems of polymer chemistry as the orientation of molecules during chain growth (stereoregulation), the creation of mild conditions of polymerisation, and the absence from the polymer of initiator fragments, which might in time cause degradation of the latter[9].

By no means all the potentialities of electrochemical initiation have been studied. Obviously for this reason it has not yet become so widespread as other, less controllable methods of initiation. However, the progress which has been achieved in replacing chemical initiation of the polymerisation of certain monomers, in particular halogenated alkenes[6,7], and the possibility of obtaining crystalline polymers during electrolysis[5,10], provide grounds for believing in the prospects for electrochemical initiation. This is perhaps the only electrochemical process in which considerably more than one mole of substance is transformed per faraday of electricity. The efficiency of the electrochemical reaction can be measured by the mean molecular weight of the resulting polymer.

A considerable number of publications have now appeared on the electrochemical initiation of polymerisation, but, apart from brief surveys mainly of the radical polymerisation of certain monomers[11-13], of dimerisation[14], and of a very narrow field[15], no papers of a review character have been published. Nevertheless, Breitenbach[16-18], Funt[19-23], Yamazaki[24], Parravano[25], and Soviet workers[26,27] have recently reported investigations of the electrochemical initiation of ionic polymerisation, in particular the preparation of "living" polymers[22-27]. Careful analysis of work on electrochemical initiation is urgently necessary in order to discuss the possibilities, merits, and defects of this method.

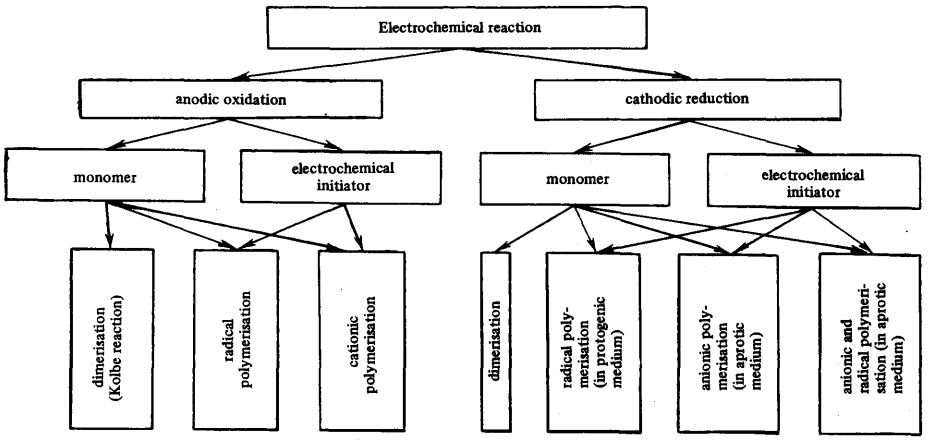
The polymer chain grows by a radical or an ionic mechanism depending on the conditions, and is little affected by whether initiation is electrochemical or chemical. The character of electrochemically initiated polymerisation is primarily determined by the mechanism and the rate of the electrode reaction. In the present Review, therefore, attention will be paid mainly to investigations of the mechanism and the kinetics of the electrode process and of the accompanying chemical reactions. From these data we can predict the yield of initiating species and of byproducts (resulting from dimerisation or complete reduction of the double bond), the accumulation of which prevents polymerisation.

II. CLASSIFICATION OF METHODS FOR THE ELECTROCHEMICAL INITIATION OF POLYMERISATION

Methods of electrochemical initiation can conveniently be classified according to the type of electrode process producing the initiating centres and according to the mechanism of growth of the polymer chain. Thus, depending on the type of electrode process, initiation is either anodic or cathodic; and according to the electrochemical reaction used initiation can occur either by (*a*) direct reduction or oxidation of the monomer or (*b*) oxidation or reduction of the electrochemical initiator, i.e. the compound whose anodic oxidation or cathodic reduction forms radicals or radical-ions capable of initiating polymerisation[10]. Radical and ionic (cationic or anionic) polymerisation processes are distinguished by the mechanism of chain growth. On the basis of this classification, Scheme I represents the types of electrochemical processes that have now been used for the initiation of polymerisation.

Thus the electrochemical reaction is usually a one-electron transition involving either the monomer or the electrochemical initiator. As a result active centres are formed on the electrode surface, and these are capable of

Scheme I



initiating either ionic or radical polymerisation depending on the conditions.

1. Anodic Oxidation

The direct electrochemical oxidation of organic compounds, in particular of carboxylate anions

$$C_nH_{2n+1}C(=O)O^- \rightarrow e \rightarrow C_nH_{2n+1}C(=O)O^{\cdot}\ , \qquad (1)$$

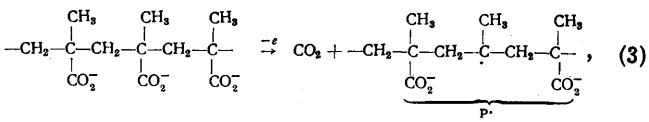
$$C_nH_{2n+1}C(=O)O^{\cdot} \rightarrow C_nH_{2n+1}^{\cdot} + CO_2\ , \qquad (2)$$

forms alkyl or alkanoxyl radicals, which then dimerise[1]. This is a particular case of electrochemical initiation—the Kolbe reaction, which has long served as a method for lengthening aliphatic hydrocarbon chains[28,29].

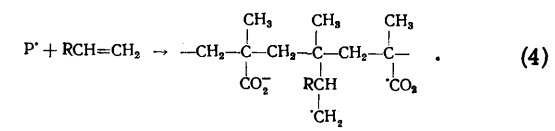
If the anodic oxidation of carboxylic acids or their salts is conducted in the presence of monomers, under appropriate conditions the radicals formed can initiate the radical polymerisation of such monomers as styrene, butadiene, isoprene, vinyl acetate, methyl methacrylate, and vinyl chloride[30-38]. Here the aliphatic acids and their salts undergoing oxidation at the anode are the electrochemical initiators.

Salts of metals of variable valency, in particular nickel(II) and manganese(II), can also be used as electrochemical initiators during anodic oxidation; Koval'chuk suggests[39,40] that during their electrolysis polymerisation is initiated by π-complexes with the monomer (e.g. acrylamide) of the metal in a higher valency state. Formation of such complexes is most probable on the adsorption at the electrode surface of a monomer whose double bond is polarised. Polymerisation can be initiated also by electrochemical oxidation of the sulphate anion, which may yield the radical-anion $SO_4^{\cdot-}$, capable of initiating polymerisation[41].

The use of macromolecular acids as electrochemical initiators is of undoubted interest. Thus the macroradicals of polymethacrylic acid obtained by anodic oxidation are able to interact with monomers[42]:



(3)



(4)

Such a reaction opens up great opportunities for modifying polymers[42,43].

In 1955 a method for the electrochemical initiation of the polymerisation of aliphatic halogenoalkenes was patented in Federal Germany[6,7].

The polymerisation of tri- and tetra-fluoroethylene initiated by peroxides takes place at high pressures (up to 100 atm) and temperatures (up to 100°C). Electrochemical initiation enables the process to be conducted at normal pressure and temperatures below 0°C. This eliminates the possibility of an explosive reaction, which at high temperatures may be caused by hot spots. Polymerisation is initiated by radicals formed at the anode during electrolysis, by F$^{\cdot}$ in hydrogen fluoride and by $CF_3^{\cdot}$ in trifluoroacetic acid. Low current densities enable the radicals to react with the monomer:

$$CF_3^{\cdot} + CF_2{=}CF_2 \rightarrow CF_3{-}CF_2{-}CF_2^{\cdot}\ . \qquad (5)$$

At low temperatures and high monomer concentrations chain growth can then occur with formation of a product of relatively high molecular weight[7].

If the radical formed by oxidation of the electrochemical initiator possesses high electron affinity, it may oxidise the monomer, which will lead to the initiation of cationic polymerisation[17].

2. Cathodic Reduction

A cathodic process results in formation of the initiating species both by direct reduction of the monomer and by reduction of the electrochemical initiator. The mechanism of growth of the polymer chain depends on the conditions. Thus direct electrochemical reduction of a monomer in a protogenic medium leads to formation of a radical (a protonated radical-anion) that initiates radical polymerisation [44-49], whereas in an aprotic medium anionic polymerisation takes place [5,17-22,50-53]†. Furthermore, simultaneous growth of the polymer chain by anionic and radical mechanisms is also possible during the early stages in an aprotic medium [8,20]. In several cases either an anionic or a mixed mechanism can be realised by conducting polymerisation in an aprotic medium and using cathodic reduction of an electrochemical initiator, in particular an alkali-metal ion [20].

The first electrochemical initiator of radical polymerisation to be used was the hydrogen ion [3,4,54,55], which on cathodic reduction causes the polymerisation of such monomers as methyl methacrylate, acrylic acid, vinyl acetate, etc. [56,57] According to the recombination theory of hydrogen overpotential [58] the efficiency of initiation depends on the electrode material and is a function of the overpotential [54]. Parravano [54,56] suggested that the initiating action of hydrogen atoms obtained electrolytically was analogous to their behaviour when adsorbed on a metal surface:

$$MH + R \rightarrow {}^{\cdot}RH + M \ . \qquad (6)$$

Mairanovskii [59] showed that a more probable mechanism in acid media is reduction of an already protonated monomer molecule, which as a result of the electrochemical process becomes the initiating agent [60,61]:

$$RH^+ + e \rightarrow {}^{\cdot}RH \ . \qquad (7)$$

This mechanism is supported by a phenomenon observed in the polarographic investigation of acrylamide [62]. This compound facilitates the electrochemical reduction of hydrogen, whose half-wave potential becomes more positive in the presence of this monomer, whereas that of acrylamide itself is independent of pH. [63] Thus, in the formation of a radical capable of initiating polymerisation, it is not the proton but the complex RH^+ that is reduced:

$$H^+ + R + e \rightarrow {}^{\cdot}RH \ . \qquad (8)$$

On the basis of views developed by Antropov [64] it can be concluded that the potential-determining stage is reaction (8), whose rate, according to the slow discharge theory [58], is given by

$$i = kC^S_{H^+}C^S_R \exp\left(-\frac{\alpha nFE}{RT}\right) \qquad (9)$$

where i is the current, k is the rate constant of reaction (8), $C^S_{H^+}$ and C^S_R are the surface concentrations of protons and of acrylamide, α is the transfer coefficient of the electron (~ 0.5), F is Faraday's constant, and $n = 1$ is the number of electrons. Since the hydrogen diffusion current i_d remains unchanged in the presence of acrylamide, a definite concentration of the monomer, proportional to its concentration C_R in the solution, can be assumed to be present on the electrode surface:

$$C^S_R = k'C_R \ . \qquad (10)$$

Then

$$E = E_0 + \frac{2RT}{F}\ln\frac{C_{H^+}}{i_d} + \frac{2RT}{F}\ln k'C_R - \frac{2RT}{F}\ln\frac{i}{i_d - i} \ , \qquad (11)$$

whence

$$E = E_{1/2} + 0.118\lg\frac{i}{i_d - i} \ , \qquad (12)$$

where

$$E_{1/2} = \text{const} + 0.118\lg C_R \ . \qquad (13)$$

The experimental slope of this relation is close to the theoretical value (0.125 and 0.118 respectively).

The electrochemical reduction of oxygen can be used to initiate radical polymerisation [65]. Fedorova et al. [65] showed that the first stage involves the formation of hydrogen peroxide:

$$O_2 + e + H^+ \rightarrow HO_2 \ , \qquad (14)$$

$$HO_2 + e + H^+ \rightarrow H_2O_2 \ . \qquad (15)$$

This is then reduced to water:

$$H_2O_2 + e \rightarrow {}^{\cdot}OH + HO^- \ , \qquad (16)$$

$$HO^- + H^+ \rightarrow H_2O \ , \qquad (17)$$

$$^{\cdot}OH + e + H^+ \rightarrow H_2O \ . \qquad (18)$$

The radical $HO^{\cdot}$ formed as intermediate is able to initiate the polymerisation of methyl methacrylate and other derivatives of acrylic acid [66].

Radical polymerisation in aqueous medium can be initiated by a redox system in which the product of the cathodic reduction of one component reacts with the second component to form the initiating radicals [66]. An example is the cathodic reduction of tervalent iron in the presence of a peroxide:

$$Fe^{3+} + e \rightleftarrows Fe^{2+} \ , \qquad (19)$$

$$Fe^{3+} + H_2O_2 \rightleftarrows Fe^{3+} + OH^- + {}^{\cdot}OH \ , \qquad (20)$$

or

$$Fe^{3+} + S_2O_8^{3-} \rightleftarrows Fe^{3+} + SO_4^{3-} + SO_4^{\cdot-} \ , \qquad (21)$$

The radical $HO^{\cdot}$ and the radical-ion $SO_4^{\cdot-}$ are able, as Kolthoff showed [66], to initiate the polymerisation of acrylic monomers:

$$^{\cdot}OH + R \rightarrow HOR^{\cdot} \ , \qquad (22)$$

$$SO_4^{\cdot-} + R \rightarrow {}^{-}SO_4 - R^{\cdot} \ . \qquad (23)$$

Furthermore, a redox system can be established in which a cathode acts as reductant, while the oxidant is converted during reduction into an active polymerisation initiator [67,68]. The advantage of such a system in comparison with the preceding system is the possibility of controlling the rate of formation of initiating centres by eliminating intermediate stages.

Thus quite a wide range of reactions can now be used for the electrochemical initiation of polymerisation.

Since one of the main advantages of electrochemical initiation is the possibility of controlling the rate of polymerisation by varying the current density, we must

† The radical mechanism suggested originally [52,53] for the polymerisation of acrylonitrile in an aprotic medium with electrochemical initiation was subsequently revised. The absence of an inhibiting effect by diphenylpicrylhydrazyl and also experiments on the copolymerisation of acrylonitrile (study of the composition of the copolymers) established that polymerisation takes place by an ionic mechanism under these conditions [16,17].

examine in greater detail how this possibility is realised, starting not only from the mechanism of the electrode process but also from that of polymerisation as a whole.

III. RADICAL POLYMERISATION

1. Direct Electrochemical Reduction (Oxidation) of the Monomer

The simplest case of the electrochemical initiation of radical polymerisation in a protogenic solvent is direct cathodic reduction of the monomer. The first stage in this process is the actual electrochemical formation of the radicals capable of initiating polymerisation:

$$R + e + H^+ \underset{k_2}{\overset{k_1}{\rightleftarrows}} HR^\cdot . \qquad (24)$$

The rate of reaction (24) can be expressed[69] in terms of the current:

$$v = \gamma i = k_1 [R][H^+] \exp\left(-\frac{\alpha\varphi F}{RT}\right) - k_2 [^\cdot RH] \exp\frac{\beta\varphi F}{RT} , \qquad (25)$$

where φ is the electrode potential, α the transfer coefficient of the electron for the cathodic process, $\beta = 1 - \alpha$ the transfer coefficient for the anodic process, and γ (moles amp^{-1} cm^{-1} s^{-1}) a coefficient of proportionality. Formation of $^\cdot$RH radicals is immediately followed by three parallel reactions, whose rates are limited by the rate of generation of these radicals—(i) recombination of the radicals on the electrode surface

$$^\cdot RH + {}^\cdot RH \underset{k_4}{\overset{k_3}{\rightleftarrows}} HR{-}RH , \qquad (26)$$

at a rate

$$v_1 = k_3 [^\cdot RH]^2 - k_4 [H{-}R{-}R{-}H] ; \qquad (27)$$

(ii) further electrochemical reduction of $^\cdot$RH at the same potential (an organic radical undergoes electrochemical reduction more readily than does the molecule from which it has been formed[70])

$$^\cdot RH + e + H^+ \underset{k_6}{\overset{k_5}{\rightleftarrows}} RH_2 , \qquad (28)$$

at the rate

$$v_2 = \gamma i_2 = k_5 [^\cdot RH][H^+] \exp\left(\frac{-\alpha\varphi F}{RT}\right) - k_6 [RH_2] \exp\frac{\beta\varphi F}{RT} ; \qquad (29)$$

(iii) actual initiation of polymerisation—reaction of HR$^\cdot$ with the monomer

$$HR^\cdot + R \underset{k_8}{\overset{k_7}{\rightleftarrows}} HR{-}R^\cdot , \qquad (30)$$

at the rate

$$v_3 = k_7 [^\cdot RH][R] - k_8 [^\cdot R{-}RH] . \qquad (31)$$

Since reactions (24), (26), (28), and (30) are irreversible[71,72], so that $k_2 = k_4 = k_6 = k_8 \to 0$, the second term on the right-hand side of Eqns. (25), (27), (29) and (31) can be neglected.

Thus, under otherwise similar conditions, both the actual rate of initiation and the yield of polymer depend on the rates of reactions (24) and (30), which in turn are determined by the electrode potential φ, the concentration of active centres HR$^\cdot$, and the concentration of the monomer R. However, increasing the rate of reaction (24) by raising the electrode potential (increasing the current density) leads to the accumulation of radicals HR$^\cdot$ on the electrode surface, i.e. to an increase in the rates of reactions (26) and (28), which result in deactivation of the initiating species and hence decrease the rate of initiation and the polymer yield (after a certain time of electrolysis).

Radicals formed by cathodic reduction tend to be adsorbed, as a consequence of the presence of the unpaired electron[73]. The monomer can be assumed to react with the radical on the electrode surface, occupying unfilled sites on the latter. We express the surface concentration of radicals HR$^\cdot$ in terms of the surface coverage θ, and that of the monomer [RS] in terms of its bulk concentration [R] and surface coverage:

$$[^\cdot RH] = f\theta , \qquad (32)$$

$$[R_S] = \varkappa [R](1-\theta) , \qquad (33)$$

where f and κ are proportionality coefficients. Equating to zero the second terms in Eqns. (25), (27), (29), and (31), and substituting for [$^\cdot$RH] and [RS], we obtain

$$v = k_1^* [R](1-\theta)[H^+] \exp\left(-\frac{\alpha\varphi F}{RT}\right) ,$$

$$v_1 = k_3^* \theta^2 , \qquad (35)$$

$$v_2 = k_5^* \theta [H^+] \exp\left(-\frac{\alpha\varphi F}{RT}\right) , \qquad (36)$$

$$v_3 = k_7^* \theta (1-\theta)[R] , \qquad (37)$$

where the k^* are rate constants allowing for f and κ.

The yield η of the polymer can be written provisionally as the ratio of the rate of reaction (30) to the sum of the rates of the parallel reactions (26), (28), and (30):

$$\eta = \frac{v_3}{v_1 + v_2 + v_3} . \qquad (38)$$

Then

$$\eta = \frac{k_7^* (\theta)(1-\theta)[R]}{k_3^* \theta^2 + k_5^* \theta [H^+] \exp\left(-\frac{\alpha\varphi F}{RT}\right) + k_7^* \theta (1-\theta)[R]} = \frac{k_7^* (1-\theta)[R]}{k_3^* \theta + k_5^* [H^+] \exp\left(-\frac{\alpha\varphi F}{RT}\right) + k_7^* (1-\theta)[R]} . \qquad (39)$$

Or, starting from formulae (25), (27), (29), and (31) with the assumptions adopted, we have

$$\eta = \frac{k_7 [^\cdot RH][R]}{k_3 [^\cdot RH]^2 + k_5 [^\cdot RH][H^+] \exp\left(-\frac{\alpha\varphi F}{RT}\right) + k_7 [^\cdot RH][R]} = \frac{k_7 [R]}{k_3 [^\cdot RH] + k_5 [H^+] \exp\left(-\frac{\alpha\varphi F}{RT}\right) + k_7 [R]} . \qquad (40)$$

Equations (39) and (40) show that the yield of polymer decreases with increase in electrode potential, the hydrogen-ion concentration, the free-radical concentration, and hence the surface coverage of the electrode. In fact the dependence of polymer yield on current density obtained by Funt[74] for the electrochemical initiation of the polymerisation of *N*-vinylpyrrolidone approaches zero asymptotically (Fig. 1). The dependence of polymer yield on monomer concentration established in this work (Fig. 2) also agrees well with Eqn. (40).

It is easy to show that, since the rate constant of the recombination of radicals k_3 is usually $\sim 10^7$–10^8 M^{-1} s^{-1},[72] the yield of polymer is insignificant even at low current densities. This is confirmed also by experimental results obtained by Dineen et al.,[3] Palit and Das[56], and Parravano[54] for the cathodic initiation of the polymerisation of various derivatives of acrylic acid, and also by Funt for the electrochemical initiation of the polymerisation of *N*-vinylpyrrolidone[74].

The radical polymerisation of acrylamide also proceeds similarly during its direct electrochemical reduction[45]. Two schemes were suggested to describe the mechanism, and explained satisfactorily the observed reactions of acrylamide (R). According to the first scheme (II) the interaction of two radical-anions leads to anionic polymerisation, which can develop only in an anhydrous medium. According to the second scheme (III) addition of a proton leads to formation of the radical HR$^{\cdot}$, which is capable either of initiating polymerisation or of recombining with formation of a dimer. Experiment showed[46] that the yield of polymer was negligible. Minute quantities (around 2–3 mg) of polyacrylamide were formed as a thin, water-insoluble film on the cathode surface.

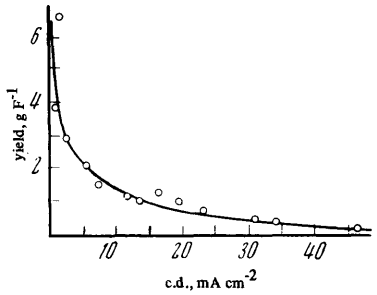


Figure 1. Effect of current density on current efficiency of polyvinylpyrrolidone formation[74].

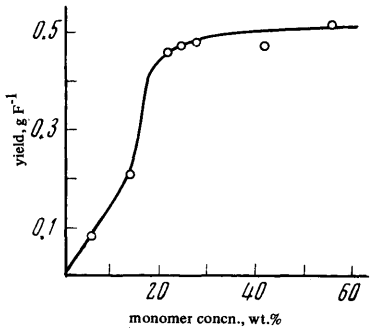


Figure 2. Dependence of yield of polyvinylpyrrolidone on monomer concentration with electrochemical initiation[74].

Another reason for such a low yield of polymer may be that the acrylamide dimers, trimers, or tetramers formed by recombination of the radicals or their interaction with the monomer diffuse slowly into the bulk of the solution, screening the electrode surface and thereby preventing transport of the monomer. Possible experimental support for this may be the unusually rapid fall in the cathodic peak for acrylamide when examined by oscillographic polarography at a stationary electrode with rapid polarisation by specified alternating current[63,75]. Yet the peaks representing reduction of simple ions under the same conditions do not vary with time[76]. Stable peaks for the reduction of acrylamide can be observed only with rapid rotation of the electrode[63].

The rate of initiation of radical polymerisation can be increased by rapid rotation of the electrode, which increases the rate of supply of monomer to its surface and somewhat diminishes coverage of the surface by $^{\cdot}$RH radicals. However, adsorption of radicals cannot thereby be completely eliminated or their recombination rate constant influenced. Because of adsorption of radicals, their recombination, and adsorption of the recombination products[59], the reaction is in effect localised on the electrode surface, and the most probable process is then formation of simple or additive dimerisation products, the yield of which was shown by Tomilov and Fioshin to be proportional to the current density[13,14].

	Scheme II	Scheme III
Electrochemical stage		$R + e \rightleftarrows R^{\cdot-}$
Chemical stage (*a*) in aqueous medium	$R^{\cdot} + R^{\cdot} \rightarrow {}^{-}R-R^{-}$	$R^{\cdot-} + H_2O \rightarrow HR^{\cdot} + OH^{-}$ $HR^{\cdot} + R \rightarrow HR-R^{\cdot}$ . . . . .
(*b*) in non-aqueous medium	${}^{-}R-R^{-} + 2H_2O \rightarrow HR-RH + 2OH^{-}$	$HR^{\cdot} + HR^{\cdot} \rightarrow HR-RH$
	${}^{-}R-R^{-} + nR \rightarrow {}^{-}R-(R)_n-R^{-}$	

Since the formation of initiating radicals occurs similarly during electrochemical oxidation and reduction, the above arguments apply both to the direct cathodic reduction and to the anodic oxidation of organic compounds, the radicals of which, as a consequence of the presence of the unpaired electron, tend to be adsorbed both on positively and on negatively charged surfaces[40]. High surface coverage and large recombination rate constants k_3 are the main conditions ensuring relatively high current efficiences for the formation of dimers[77], and this has served as a basis for their industrial production[13].

Thus one of the chief advantages of electrochemical initiation—the possibility of controlling the rate of the process by varying the current density—can be exploited, in radical polymerisation effected by direct reduction of the monomer, only over a narrow range of current densities at low surface coverage of the electrode.

2. Reduction (Oxidation) of the Electrochemical Initiator

If radicals are formed as a result of cathodic reduction or anodic oxidation of an electrochemical initiator, they are adsorbed on the electrode surface, as are the monomer radicals[40]. This is followed by preferential recombination either of the primary radicals or of products formed by them with the monomer. The probability of polymer formation is very small. This is confirmed by experimental results obtained by using the reduction of hydrogen[54–57] and oxygen[65] (hydrogen peroxide) in a protogenic medium for electrochemical initiation. The rate of initiation can be described, on certain assumptions, by equations analogous to those obtained for direct reduction of the monomer. As the processes are localised in a thin layer at the electrode surface, some increase in efficiency of initiation can be achieved by rapid rotation of the electrode and the use of very highly concentrated solutions of the monomer.

In order that initiation should be accomplished in the bulk of the solution, the species formed by the electrochemical reaction must be similarly charged to the electrode. This enables the charged species to leave the

electrode surface (the surface coverage to be reduced to a minimum). On the other hand, Coulombic repulsion prevents interaction between the charged species itself and lower polymerisation products. Chain growth—reaction between charged species and the monomer—predominates, which favours formation of a polymer of high molecular weight. In the choice of initiator satisfying these requirements it is necessary that the product of its electrochemical reaction should be able to initiate polymerisation of the chosen monomer under the given conditions.

3. Initiation of Polymerisation by Electrochemical Reduction of the Persulphate Ion

Persulphates are used to initiate polymerisation of vinyl monomers in water or in aqueous–organic emulsions. Their thermal decomposition produces $SO_4^{\cdot-}$ radical-anions, which are responsible for initiation[28,72,78,79]. According to Antropov[69] and Kryukova[80] this radical-anion is formed as intermediate also in the electrochemical reduction of the persulphate ion. On the basis of this hypothesis and the above requirements for an electrochemical initiator[81] potassium persulphate was used[67,68] for the electrochemical initiation of the polymerisation of acrylamide.

In this case initiation can be represented as consisting in (i) electrochemical reduction of the persulphate ion with formation of the radical-anion

$$S_2O_8^{2-} + e \underset{k_2}{\overset{k_1}{\rightleftarrows}} SO_4^{2-} + SO_4^{\cdot-} \qquad (41)$$

and (ii) chemical reaction between the radical-anion and the monomer

$$SO_4^{\cdot-} + R \underset{k_4}{\overset{k_3}{\rightleftarrows}} {}^{-}SO_4{-}R^{\cdot} . \qquad (42)$$

Since reactions (41) and (42) are almost irreversible[79,80], it can be assumed that $k_2 \ll k_1$ and $k_4 \ll k_3$. The rate of reaction (41) can then be written

$$v_1 = \gamma \cdot i_1 = k_1 [S_2O_8^{2-}] \exp\left(-\frac{\alpha\varphi F}{RT}\right) \qquad (43)$$

and the rate of reaction (42) as

$$v_2 = k_3 [SO_4^{\cdot-}] [R] . \qquad (44)$$

With a sufficiently high monomer concentration under steady-state conditions it can be postulated that

$$v_1 = v_2 = \text{const} \qquad (45)$$

i.e. the rate of initiation is equal to the rate of electrochemical formation of the radical-ions, and hence depends on the concentration of persulphate ions and the electrode potential. However, the rate of initiation can increase with rise in potential only until the latter permits further electrochemical reduction of the persulphate radical-ion

$$SO_4^{\cdot-} + e \underset{k_6}{\overset{k_5}{\rightleftarrows}} SO_4^{2-} . \qquad (46)$$

The rate of this process (allowing for the irreversible character of the reaction) is

$$v_3 = k_5 [SO_4^{\cdot-}] \exp\left(-\frac{\alpha_1\varphi F}{RT}\right) \qquad (47)$$

where α_1 is the transfer coefficient of the second electron.

Thus the rate of formation of the polymer, and hence its yield after a certain time of electrolysis, should be proportional to the electrode potential (current density) only until the latter reaches a certain value. Further rise in potential diminishes the yield.

The experimental dependence of the yield of polyacrylamide on the cathodic current density when potassium persulphate is used as electrochemical initiator in fact passes through a maximum at a certain current density (0.04 mA cm^{-2}). The shape of the curve is almost independent of the material of the electrode[45]. Fig. 3 shows that the rate of the electrochemical polymerisation of acrylamide can be controlled by varying the current density only in the range up to 0.04 mA cm^{-2}.

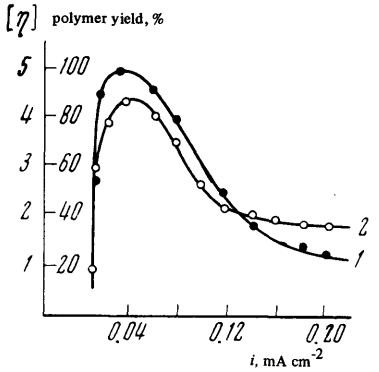


Figure 3. Effect of cathodic current density on formation of polyacrylamide: 1) yield; 2) intrinsic viscosity[45].

The dependence of the intrinsic viscosity of polyacrylamide on current density also shows a maximum. High values of the intrinsic viscosity may indicate a product of high molecular weight. The decrease in viscosity at a low current density is evidently an effect of dissolved oxygen, whose inhibiting action is apparent only at a low concentration of radicals, becoming insignificant when the concentration is considerable. One reason for the appearance of a descending section on the $[\eta]$–i curve at $i > 0.04$ mA cm^{-2} is the evolution of oxygen, which is able to interact with persulphate, acrylamide, and a growing polymer radical.

In the present case the yield of polyacrylamide at 0.03 mA cm^{-2} is proportional to the first power of the monomer concentration[45], in good agreement with Eqn. (44). A similar dependence of polymer yield on monomer concentration in solution was obtained by Funt in the electrochemical initiation of the polymerisation of vinylpyrrolidone[74] by its direct reduction (Fig. 2) (cf. also Eqn. 40).

With chemical initiation $SO_4^{\cdot-}$ radical-anions are formed not only in the thermal decomposition of persulphate ions[78] but also when the latter react with iron(II) compounds (reaction 21).[82,83] The persulphate ion then acts as oxidant in the redox process, which can be regarded as analogous to electrochemical reduction of the persulphate ion[84]. The rôle of reductant is played by the cathode, whose potential can be varied to shift the equilibrium in a required direction. When bivalent iron is used as reductant with the electrochemical initiation[66], an electrode process is necessary to maintain a certain concentration of reductant in the solution.

Thus the rate of initiation is determined by the rate of formation of active centres and the concentration of monomer with both direct and indirect (involving Fe^{2+} ions) electrochemical reduction of persulphate ions. Systems of the latter type have been successfully used by Kolthoff[66]. However, they are inferior to systems with direct electrochemical reduction of persulphate ions with respect to the possibility of controlling the rate of formation of initiating species[68].

IV. IONIC POLYMERISATION

Experience of the initiation of polymerisation by the electrochemical reduction of persulphate shows that formation of charged species by an electrode process considerably broadens the possibilities of electrochemical initiation, since it tends to spread the reaction into the bulk of the solution. However, this path provides only a partial solution of the problem of controlling the rate of the electrochemical initiation of polymerisation.

The most effective way of diminishing surface coverage of the electrode with active species is evidently to create in the polymerisable system conditions such that initiating anions would be generated on cathodic reduction, and cations by anodic oxidation, i.e. so that the initiation of ionic polymerisation would result from the electrochemical reaction. Systematic investigations in the field of ionic polymerisation have been made only during the past fifteen years[85-88], and the electrochemical initiation of such a process has been studied for barely ten years[19-25]. A few publications have appeared on the electrochemical initiation of ionic polymerisation[17-27,50-53], but the possibilities of the method and recent advances[5,23,24,26] suggest that such initiation is the most promising.

1. Cationic Polymerisation

Carbonium ions, capable of carrying the polymer chain, are formed as a result of the electrode reaction in the electrochemical initiation of cationic polymerisation[16-18]. They can be obtained by reaction of an oxidation product of the electrochemical initiator with the monomer[16] or by direct anodic oxidation of the latter[18]. Thus Breitenbach showed[16] that, when tetrabutylammonium or silver perchlorate is electrolysed in a monomer medium to which nitrobenzene has been added, polyacrylonitrile or poly-α-methylstyrene can be obtained in the anolyte by a cationic mechanism.

The suggested mechanism of initiation involves anodic oxidation of the perchlorate ion with formation of the radical $ClO_4^{\cdot}$

$$ClO_4^- \xrightarrow{k_1} ClO_4^{\cdot} + e \qquad (48)$$

and interaction between the radical and the monomer on the electrode surface to form a carbonium ion

$$ClO_4^{\cdot} + R \xrightarrow{k_2} ClO_4^- + R^+ \ . \qquad (49)$$

The carbonium ion, having like charge to the anode, passes into solution, carrying with it the polymer chain. Carbonium ions are formed similarly when the tetrafluoroborate anion is used as electrochemical initiator[53].

The rate of initiation due to oxidation of the electrochemical initiator is given by the equations

$$v_1 = k_1[ClO_4^-] \exp\frac{\beta\varphi F}{RT} \ , \qquad (50)$$

$$v_2 = k_2[ClO_4^{\cdot}][R] \ . \qquad (51)$$

In a steady state $v_1 = v_2$, and the overall rate of polymerisation is evidently determined by the rate v_1 of the electrode reaction, which varies exponentially with the electrode potential and very little with the concentration of perchlorate ions, which are regenerated by reaction (49). However, the rate of polymerisation depends strongly on the concentration of the monomer, which can be adsorbed on the electrode only until it reacts with the electrochemical initiator[40]. The cation, of like charge to the electrode, then diffuses into the bulk of the solution, where it initiates cationic polymerisation.

The second possible mode of electrochemical initiation of cationic polymerisation—direct anodic oxidation of the monomer

$$R \xrightarrow{k_1} R^+ + e \qquad (52)$$

was accomplished by Breitenbach with styrene, isobutyl vinyl ether, and *N*-vinylcarbazole[17,18].

Breitenbach compared the polarographic oxidation half-wave potentials $E_{\frac{1}{2}}$ for several monomers with the Q–e scheme of copolymerisation parameters‡.[18] The Table shows that the value of $E_{\frac{1}{2}}$ gives an idea of the mechanism of the formation of active centres during the electrochemical initiation of cationic polymerisation and copolymerisation, and also indicates the activity of monomers in this process.

Anodic oxidation potentials of some monomers in acetonitrile (rotating platinum electrode in tetraethylammonium perchlorate as supporting electrolyte; reference electrode Ag/AgCl in acetonitrile) and values of the parameter e in the Q–e scheme.

Depolariser	Oxidation potential $E_{\frac{1}{2}}$, V	e
N-Vinylcarbazole	1.14	−1.40
N-Vinylpyrrolidone	1.67	−1.14
Isobutyl vinyl ether	2.07—2.11	−1.77
Indene	1.73—1.76	−1.03
Phenylacetylene	2.12—2.30	−0.66
Styrene	1.99—2.05	−0.80
p-Methoxystyrene	1.45 1.60—1.80	−1.11
p-Methylstyrene	1.80—1.89	−0.98
p-Chlorostyrene	2.02—2.06	−0.33
α-Methylstyrene	2.00	−1.27
2-Vinylpyridine	2.72—2.80	−0.50
4-Vinylpyridine	—	−0.20
Acrylonitrile	—	+1.20
Methyl methacrylate	—	+0.40
Vinyl acetate	—	−0.22

The rate of initiation with direct oxidation of the monomer

$$v = k_1[R] \exp\frac{\beta\varphi F}{RT} \qquad (53)$$

depends on the monomer concentration and the electrode potential. An analogous relation should be observed for the yield of polymer after a certain period of electrolysis.

Although the possibility of the electrochemical initiation of cationic polymerisation has been demonstrated and

‡ Q and e are parameters in the Alfrey–Price equation, representing respectively the reactivity of the radical towards the monomer and the polarisation of the monomer molecule[89].

explained theoretically, it has been accomplished in only a few cases by Breitenbach and his coworkers[16,17,52,53] and also by Strobel and Schulz[90].

2. Anionic Polymerisation

The cathodic reduction of an electrochemical initiator in an aprotic medium—in the absence of electron-accepting impurities, in particular moisture and oxygen—followed by interaction with a monomer or the direct electrochemical reduction of the monomer to form a radical-anion leads to the initiation of anionic polymerisation[5,19-25]. Radical-anions, bearing a like charge to the cathode, are not adsorbed on its surface, but diffuse into the interior of the solution. They interact to form dianions; chain growth then takes place from the two ends by an anionic mechanism, as with chemical initiation[86,87].

(*a*) Initiation by reduction of electrochemical initiator

Electrochemically initiated polymerisation is usually accomplished in the presence of an electrically conducting additive (a tetra-alkylammonium or an alkali-metal salt). If the electron affinity of the metal ion of the additive is greater than that of the monomer, an amalgam of the metal may be obtained on the cathode during electrolysis, which will react with the monomer to form species capable of initiating anionic polymerisation:

$$M^+ + e \underset{k_2}{\overset{k_1}{\rightleftarrows}} M, \tag{54}$$

$$M + R \underset{k_4}{\overset{k_3}{\rightleftarrows}} M^+ + R^{\bar{\cdot}}, \tag{55}$$

$$R^{\bar{\cdot}} + R^{\bar{\cdot}} \xrightarrow{k_5} {}^-R{-}R^-, \tag{56}$$

$${}^-R{-}R^- + R \xrightarrow{k_6} {}^-R{-}R{-}R^-. \tag{57}$$

The rates of each stage in the process are

$$v_1 = k_1[M^+]\exp\left(-\frac{\alpha q F}{RT}\right) - k_2[M]\exp\frac{\beta\varphi F}{RT}, \tag{58}$$

$$v_2 = k_3[M][R] - k_4[M^+][R^{\bar{\cdot}}], \tag{59}$$

$$v_3 = k_5[R^{\bar{\cdot}}]^2. \tag{60}$$

The rate of the electrode reaction depends on the cathode potential and very little on the concentration of the electrochemical initiator, since metal ions are regenerated by interaction with the monomer (reaction 55).

The efficiency of initiation, which may be measured by the constant k_3 of the forward reaction (55), is determined by the difference in electron affinity between the metal M and the monomer[86-88,91]. This quantity is constant for each metal–monomer pair. Thus as a result of the electrochemical reaction we arrive in effect at chemical initiation by an amalgam of the alkali metal. However, the electrode is always negatively charged, so that anions are repelled from its surface, whereas in chemical initiation the metal amalgam may acquire a positive charge during interaction with the monomer, which will tend to attract radical-anions[92].

Control of the rate of the process, with electrochemical reduction of the metal ion, is somewhat restricted by the fixed value of k_3. In order to increase this constant it is necessary to select a metal–monomer pair such that the metal possesses a low ionisation potential, while the monomer has a high electron affinity[88,91]. Nevertheless, if the electron affinity of the monomer exceeds that of the metal ion of the electrochemical initiator, radical-anions are formed by direct cathodic reduction of the monomer[20].

(*b*) Initiation by direct reduction of monomer

The electron affinity of various compounds (in particular aromatics) varies in parallel with the half-wave potential for their polarographic reduction[93]. Thus the mechanism of formation of the active centres responsible for initiation of anionic polymerisation can be assessed in each specific system from polarographic data. If the half-wave potential for the cation of the supporting electrolyte is more negative than the half-wave potential of the monomer, electrochemical initiation of polymerisation will occur by direct reduction of the monomer[21,23,24,94] to the radical-anion

$$R + e \underset{k_2}{\overset{k_1}{\rightleftarrows}} R^{\bar{\cdot}} \tag{61}$$

whose dimerisation yields a dianion carrying the polymer chain[85,95] (reactions 57 and 61). The rate of the electrochemical stage

$$v_1 = k_1[R]\exp\left(-\frac{\alpha\varphi F}{RT}\right) - k_2[R^{\bar{\cdot}}]\exp\frac{\beta\varphi F}{RT} \tag{62}$$

is proportional to the concentration of the monomer and depends on the electrode potential φ ($k_2 \to 0$). The rate of chemical reaction of the radical-anions (Eqn. 60) is limited by their rate of formation and by Coulombic repulsion. The rate of growth of the polymer chain (reaction 57)

$$v_2^* = k_6[{}^-R - R^-][R] \tag{63}$$

is determined by the concentration of initiating dianions and the monomer. The rate of formation of the polymer (its yield after a definite time)

$$\eta = f(v_2^*) = f(v_1 + v_3) \tag{64}$$

(v_3 from Eqn. 60) is directly dependent on the electrode potential (current density), as is observed in practice (Fig. 4).

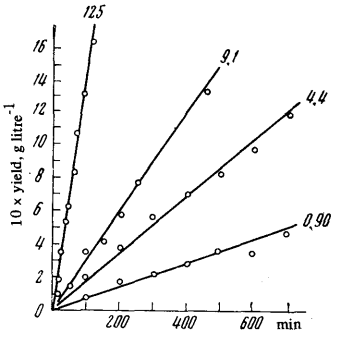


Figure 4. Dependence of yield of polyacrylonitrile on duration of reaction for various currents (mA).[21] The area of the electrode was the same (1 in^2) in all experiments.

Feoktistov and Tomilov[96,97], with acrylonitrile as example, showed that the dianion $R^=$ may be formed by direct two-electron reduction of the monomer. This mechanism is atypical of other monomers. Nevertheless, the rate of initiation and hence the yield of polymer are

determined even in this case by the electrode potential and the monomer concentration.

Thus there exist various types of electrode reactions, as a result of which either radical or ionic polymerisation occurs depending on the conditions. The above survey shows that one of the most attractive features of electrochemical initiation—the possibility of controlling the rate of polymer formation—can be successfully realised only in the initiation of ionic polymerisation. In the case of radical polymerisation ways must be sought of diminishing the surface coverage of the electrode by active species.

3. Possibilities of Simultaneous Radical and Ionic Mechanisms of Chain Growth with Electrochemical Initiation

A radical-anion formed by reaction (55) or (61) has an unpaired electron in the lowest vacant π-orbital[85] of the monomer. This electron is usually delocalised, so that the recombination of monomeric radical-anions (reaction 56) is, according to Szwarc[85,86] and to Bagdasar'yan[98], the slowest stage in the initiation of anionic polymerisation and limits the overall rate of polymerisation. Funt reaches a similar conclusion from an investigation of the electrochemical initiation of the anionic polymerisation of acrylonitrile[21].

At a sufficiently high monomer concentration (at the electrode surface) reactions (61) and

$$R^{\cdot-} + R \xrightarrow{k_5} {}^{\cdot}R{-}R^{-} \qquad (65)$$

can evidently occur consecutively. This involves stabilisation of anionic and radical ends, after which the dimeric radical-anions may undergo recombination

$${}^{\cdot}R{-}R^{-} + {}^{\cdot}R{-}R^{-} \xrightarrow{k_6} {}^{-}R{-}R{-}R{-}R^{-} \qquad (66)$$

and chain growth by an anionic mechanism; in the limiting case the chain may grow at the two ends simultaneously by radical and anionic mechanisms

$${}^{\cdot}R{-}R^{-} + R \xrightarrow{k_7} {}^{\cdot}R{-}R{-}R^{-}. \qquad (67)$$

The possibility of such a process was postulated by Tobolsky et al. in the polymerisation of styrene initiated by metallic sodium[99] and by Funt et al.[21] under conditions of electrochemical initiation. The latter workers discovered that the composition of a copolymer of acrylonitrile with methyl methacrylate or styrene indicates that a radical mechanism of polymerisation predominates at the start of electrolysis (polymerisation), and an anionic mechanism as time elapses.

The possibility of the simultaneous addition of monomer molecules to anionic and radical ends of a radical-ion has been confirmed by experiments on the inhibition of the electrochemically initiated polymerisation of acrylonitrile in dimethylformamide[8,95]. Such chain-transfer agents for radical polymerisation as benzene, toluene, and chlorobenzene, which can be adsorbed on the electrode[100], partly inhibit the cathodic polymerisation of acrylonitrile, diminishing the yield of polymer by ~ 20%, whereas they completely inhibit anodic polymerisation (a purely radical process).

It is difficult to determine the rate of reactions (65) and (66). Since, however, k_5 evidently exceeds k_6, and the rate of chain growth by anionic polymerisation at low temperatures and in the absence of impurities considerably exceeds the rate of growth by radical polymerisation, the total rate of polymerisation can be assumed to be determined by the electrode potential and the monomer concentration, as in anionic polymerisation.

4. Electrochemical Initiation of the Anionic Polymerisation of Isocyanates

The electrochemical initiation of anionic polymerisation can be most conveniently studied on monomers that cannot be polymerised by any other mechanism. A classic example of this is phenyl isocyanate, which can be polymerised only by an anionic mechanism[101-103]. The possibility of the electrochemical reduction of phenyl isocyanate has been shown polarographically[104]. On reduction at a dropping mercury electrode in dimethylformamide this compound gives a single polarographic wave representing the addition of two electrons by the reactions

$$R + e \rightarrow R^{\cdot-}, \qquad (68)$$

$$R^{\cdot-} \xrightarrow{PD} {}^{\cdot}RH, \qquad (69)$$

$${}^{\cdot}RH + e \rightarrow {}^{-}RH, \qquad (70)$$

$${}^{-}RH \xrightarrow{PD} RH_2, \qquad (71)$$

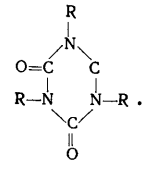
(where PD represents a proton donor).

This mechanism is possible at low concentrations of phenyl isocyanate, when sufficient hydrogen ions are present at the electrode surface to protonate the reduced molecule§. At considerable concentrations of the isocyanate ([R] ≫ [H_2O]) its wave divides into two. The second wave corresponds to addition of an electron to the radical-anion at a more negative potential:

$$R^{\cdot-} + e \rightarrow R^{=} \qquad (72)$$

With increase in the isocyanate concentration, however, the second wave does not grow but diminishes: the total height of the waves approaches the height of a one-electron wave, so that the number of added electrons n changes from 2 to ~ 1. The reason is that the radical-ions of phenyl isocyanate recombine to form a bianion (reaction 56), which is able to initiate polymerisation.

These results suggest that electrochemical initiation of the anionic polymerisation of phenyl isocyanate can occur at a monomer concentration of 0.02 M and an electrode potential (current density) corresponding to the potential of its first wave. Electrolysis of a solution of phenyl isocyanate in an aprotic medium in fact yields a polymer[5] corresponding in properties to the poly(phenyl isocyanate) obtained by the action of anionic catalysts[101,103]. The suggested mechanism of electrochemical initiation by direct reduction of the monomer with cleavage of the N=C bond is confirmed by the elementary composition and the infrared spectra of the resulting poly(phenyl isocyanate) and by the formation, under the same conditions at room temperature, of the trimer[105,106]



The yield of polymer increases with fall in temperature, increase in monomer concentration, and decrease in

§ Karl Fischer's method indicates that well dehydrated dimethylformamide contains 0.01% of moisture, corresponding to a concentration of ~ 0.005 M: i.e. the quantity of water is comparable with the concentration of depolariser.

current density[10,107], which agrees well with the general laws of anionic polymerisation with chemical initiation. The increase in polymer yield with decrease in current density observed in this work appears at first glance to be inconsistent with Eqn. (62) for the rate of electrochemical formation of the active centres responsible for the initiation of anionic polymerisation. The explanation is that at a high current density the rate of formation of the cyclic trimer of phenyl isocyanate by an anionic mechanism increases, which lowers the rate of initiation of actual polymerisation. Isocyanates are known to tend to form trimers[101,102].

Special stress must be laid on the crystallinity of the poly(phenyl isocyanate) obtained by electrochemical initiation: i.e. it has a regular structure, as indicated by the coincidence of its X-ray patterns with those of the polymer obtained by Natta[101] using stereospecific catalysts. With chemical initiation the crystallinity of the polymer is strongly dependent on the solvent, gegenion, and temperature[108]. With electrochemical initiation crystalline poly(phenyl isocyanate) was obtained in such solvents as dimethylformamide, oxolan, and acetone in the presence and in the absence of tetrabutylammonium iodide.

All this is evidence that, with electrochemical initiation, stereoregularity is largely achieved by orientation of monomer molecules on the electrode surface in the initial stages of growth of the polymer chain. Thus with phenyl isocyanate as example it has been shown for the first time that stereospecific polymerisation is fundamentally possible with electrochemical initiation.

5. Preparation of "Living" Polymers by Electrochemical Initiation

During the 1960s so called "living" polymers aroused the special interest of scientists in the field of anionic polymerisation. Such polymers were first obtained by Szwarc[91] by polymerising α-methylstyrene in a non-polar medium under the influence of metallic sodium or an alkali-metal alkyl[85,86]. Great advances in the field of anionic polymerisation were made by Soviet investigators—Medvedev's school[109-112], Bagdasar'yan[98], Erusalimskii[113,114], Enikolopyan[115,116], and Lipatova[117]. A "living" polymer is brightly coloured owing to the presence of the ion-pairs $\sim CH_2CHAr^-M^+$ at the ends of the macromolecules (M = Na, Li). Fresh portions of a monomer undergo polymerisation when added to a solution of a "living" polymer. Polymers obtained in this way have a narrow molecular-weight distribution.

Electrochemical initiation of polymerisation, as a result of which "living" polymers are obtained, allows either the number of active centres to be changed during polymerisation or their rate of formation to be maintained constant, in addition to the general opportunities available with chemical initiation.

Furthermore, increasing attention has been paid during recent years to polymers (oligomers) having definite functional terminal groups. They are usually obtained by adding to a solution of a "living" polymer compound which react with the "living" carbanion to form new functional groups at the ends of the macromolecule[91]. Thus the addition of proton donors results in the appearance of hydrogen at the ends of a polymer chain, carbon dioxide yields a carboxy-group, oxiran produces a hydroxyl, etc.

A virtue of electrochemical polymerisation is the possibility of deactivating "living" polymers by changing the polarity of the electrodes, i.e. the possibility of obtaining terminal groups of a polymer by interaction of the products of anodic and cathodic reactions[23]:

$$^-R{-}R_n{-}R^- + 2R_1^+ \rightarrow R_1{-}R_{n+2}{-}R_1 \quad (73)$$

This feature of electrochemical initiation opens up new routes for the synthesis of macromolecules having specified terminal groups.

Yet another important advantage is that electrochemical initiation enables "living" radical-anions to be obtained by direct cathodic reduction of the monomer, eliminating the stage of preparation of a catalyst, which is especially sensitive to contamination by moisture and oxygen[91].

(*a*) Preparation of linear "living" polymers

Especially clean conditions—absence of contamination and of impurities of proton-donating and electron-accepting character—are required to obtain "living" polymers by an anionic mechanism. Electrochemical "living" poly-α-methylstyrene was first obtained in 1965 by Yamazaki et al.,[24] who electrolysed a solution of the monomer in oxolan in the presence of lithium tetrahydroaluminate and a sodium tetra-alkylaluminate. This polymer had a bright cherry-red colour and a quite high molecular weight. Values found for the molecular weight were close to those calculated by means of the formula[23]

$$M_n = \frac{[M]}{0.5I} \quad (74)$$

(I is the number of faradays of electricity and [M] the concentration of the monomer), which was deduced on the assumption that polymerisation was initiated by dianions formed by recombination of radical-anions produced initially (i.e. it was assumed that two electrons were consumed in the formation of one macromolecule).

The bright colour of the styrene carbanions formed by electrolysis enables the rate of formation of active centres to be followed from the variation in the absorption maximum (λ_{max} = 340 nm) in the electronic spectrum, and their rate of disappearance from the change in polarisation of the electrodes.

The possibility of obtaining "living" polymers in liquid ammonia by the electrochemical initiation of anionic polymerisation is especially noteworthy. Thus Parravano et al.[25] electrolysed 4-vinylpyridine in liquid ammonia, and obtained in quantitative yield at the cathode a polymer of molecular weight $(6-10) \times 10^4$ and a quite narrow molecular-weight distribution (M_W/M_n = 1.5). In this case initiation takes place in the bulk of the solution, by addition of a so called "solvated" electron to the monomer, which involves formation of radical-anions and their recombination products—bianions. Current efficiencies of 0.5 mole F^{-1} are cited as evidence of the suggested mechanism.

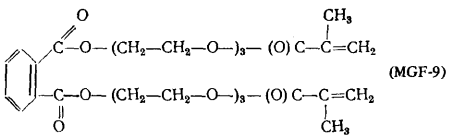
Experiments in which polymerisation occurred after addition of a second portion of the monomer, without further electrolysis, confirm that the polymer obtained is "living".

(*b*) Preparation of network "living" polymers

If a monomer contains two or more double bonds, a three-dimensional network polymer is formed, which under certain conditions may be "living". Lipatova and Siderko obtained such "living" network polymers by anionic polymerisation with chemical initiation from oligo(ether-acrylates).[117] These compounds contain reducible groups

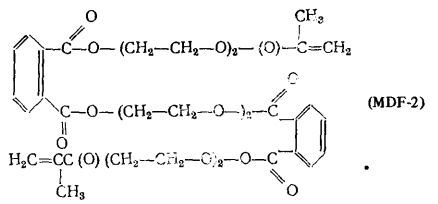
(phthalate and methyl methacrylate[118]) differing in electron affinity and separated by a system of σ-bonds. All this makes them interesting both with regard to the laws of anionic polymerisation itself and with regard to the mechanism of their electrochemical reduction and the formation, during the electrochemical reaction, of the active centres responsible for the initiation of polymerisation.

The possibility of obtaining "living" network polymers from oligo(ether–acrylates) by electrochemical initiation was established in the cases of bismethacryloyloxyethoxyethyl phthalate (MGF-9)



(MGF-9)

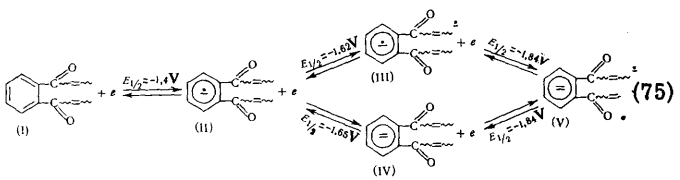
and oxadiethylene bis(methacryloyloxyethoxyethyl phthalate) (MDF-2)¶



(MDF-2)

It is especially noteworthy that a "living" polymer can be obtained by electrochemical initiation from an oligo(ether–acrylate) not only under a high vacuum (with oxolan as medium), as in the electrochemical polymerisation of styrene[23,24], but also in such a highly polar solvent as dimethylformamide (with addition of tetrabutylammonium iodide and a current of argon)[25,119,120].

Investigation of the mechanism of the electrochemical reduction of oligo(ether–acrylates) by polarography and oscillographic polarography with a specified alternating current and the use of model compounds (methyl methacrylate and dimethyl phthalate) shows that the transfer of electrons to the oligomer molecule is a stepwise process, characterised by three diffusion waves[121], and each electrochemically active group is reduced independently of the others[27]. From the half-wave potentials of the functional groups in the oligomer the electrochemical reduction of MGF-9 can thus be represented[27]



(75)

Products (III) and (V) are able to initiate anionic polymerisation, whereas the products of the one- and two-electron reduction of the phthalate group in the oligomer (II and IV respectively) do not cause polymerisation, although the solution on electrolysis has the bright colour characteristic of the radical-ion or the dianion of dimethyl phthalate.

Thus the electrochemically reduced oligo(ether–acrylate) molecules carry 1–3 negative charges. On the one hand this causes repulsion from the cathode of similarly charged species, i.e. the occurrence of polymerisation in the bulk of the solution; on the other hand, it promotes formation of a polymer network from previously uncoiled oligomeric blocks, which in turn produces a certain (fibrillar) supermolecular structure in the polymer, as is confirmed by electron microscopy[122].

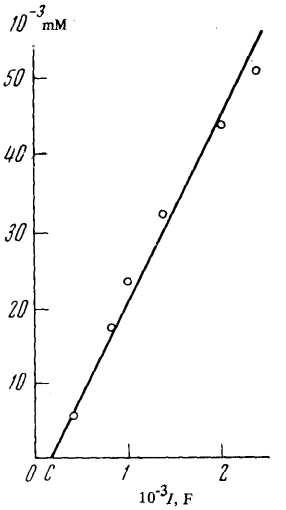


Figure 5. Dependence of yield of network poly(ether–acrylate) on quantity of electricity that has passed through 0.5 M solution of MGF-9 oligo(ether–acrylate) in dimethylformamide[120].

Features of the mechanism of the electrochemical initiation of polymerisation associated with the specific structure of oligo(ether–acrylates) affect the dependence of polymer yield on the quantity of electricity that has passed through the oligomer solution. According to Eqn. (64) the yield of polymer with electrochemical initiation of anionic polymerisation is proportional to the monomer concentration and to the quantity of initiating particles formed by the electrode reaction (to the electrode potential). In the present case the yield is actually proportional to the concentration of oligo(ether–acrylate). Nevertheless, the dependence of the yield of poly(ether–acrylate) on the quantity of electricity that has flowed through the solution is a straight line not passing through the origin (Fig. 5). The reason is that part of the electricity is consumed in charging the oligomer molecules (formation of products II and IV in reaction 75), which confirms the suggested scheme of electrochemical reduction of these compounds. The straight line is represented by the equation

$$\eta = K(I - I_{thr}), \qquad (76)$$

where η (expressed as molarity of oligomer that has reacted) is the yield of polymer, I (F) the quantity of electricity that has passed through during electrolysis, I_{thr} the minimum quantity of electricity necessary for polymerisation of the oligomer to begin under the given conditions (the intercept O–C made by the straight line in Fig. 5), which is termed a "threshold" by analogy with Lipatova and Siderko's "threshold" catalyst concentration[117], below which the anionic polymerisation of oligo(ether–acrylates) under the influence of sodium naphthalene does not take place, although the solution is

¶ Notation of oligo(ether–acrylates) taken from Ref. 118.

coloured, and K a constant representing the efficiency of the electrochemical reaction—the number of moles of the oligomer converted under the given conditions by one faraday of electricity. The value of K determined in the electrochemical initiation of the polymerisation of MGF-9 is 23.5 moles F^{-1}, indicating that the electrochemical reaction is highly efficient.

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With electrochemical initiation the electrode process is thus the source of the active centres responsible for initiating polymerisation. This allows their rate of generation to be controlled, the mechanism to be determined, and aspects of initiation to be examined in the formation of both linear and network polymers. On the other hand, the field of the electrode affects the growth of the polymer chain. The carbanion or carbonium cation carrying the chain interacts with monomer molecules already oriented in the field of the electrode. This determines the structure and the physicochemical properties of the polymers. Several publications have appeared on electrochemical initiation[122-138] while the manuscript was being prepared for the press.

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